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AGING AND DEGRADATION OF POLYOLEFINS
IV. PHOTODECOMPOSITIONS OF MODEL PEROXIDES

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Stanford Research Institute

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For the Period June 1, 1969 to August 31, 1972

Report No. 12 for Project 8012-1

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STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

For the Period June 1, 1969 to August 31, 1972

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AGING AND DEGRADATION OF POLYOLEFINS

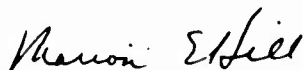
IV. Photodecompositions of Model Peroxides

By: THEODORE MILL, HAROLD RICHARDSON, and FRANK R. MAYO

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Sections 1,2,3, part of 4, and 7 are new material added to Draft Final Report No. 8.

PHOTODECOMPOSITIONS OF MODEL PEROXIDES

1. OBJECTIVE

Previous reports in this series have discussed in detail the mechanism of free radical oxidation of atactic polypropylene (APP) in the dark. The objective of this research is to evaluate the importance of some photochemical oxidation and cleavage reactions involved in the degradation of polypropylene.

2. SUMMARY

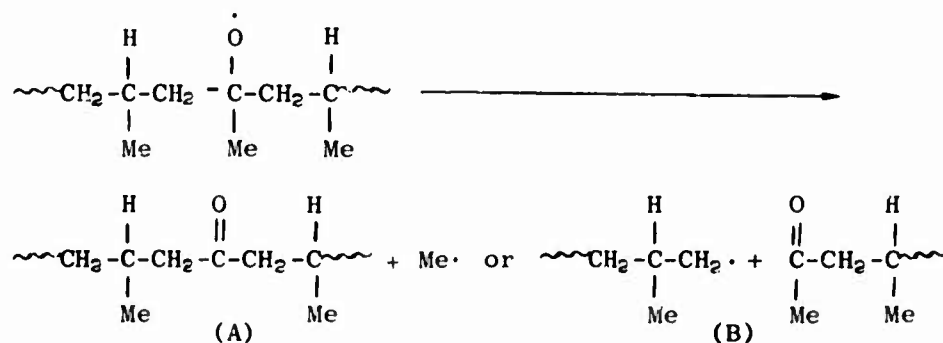
There appear to be no unusual effects of phase change or near uv radiation on the reactions of alkoxy radical models for APP. The oxidation of purified APP by singlet oxygen is not an important process at 50° (Section 5). Photochemical and thermal cleavages of t-amylloxy radicals, a model for polypropylene oxy radicals, give nearly the same ratio of k_a/k_d at 50° (Section 6). Photochemical cleavage of the model compound 1,1-dinonylethyl hydroperoxide (10-methyl-10-nonadecyl hydroperoxide) gives exclusive cleavage of a nonyl group both in solution and in polypropylene film at 50° (Section 7). This result raises doubts about reports of cleavage of methyl radicals from tertiary alkoxy radicals in polypropylene.

3. BACKGROUND

Photodegradation of polymers is generally thought to proceed by a combination of free-radical and photolytic reactions initiated by thermolysis of peroxides and by photolysis of peroxides and carbonyl

groups. The importance of singlet oxygen in photodegradations of polyolefins is uncertain. Trozzolo and Winslow¹ proposed that carbonyl groups in polyethylene, excited by near uv light, cleave to give methyl ketones and terminal vinyl groups and also excite molecular oxygen to the singlet state. Singlet oxygen might then react with the vinyl groups to give allylic hydroperoxides and further oxidation. The importance of singlet oxygen should then depend on the concentration of carbonyl groups and on the resulting free radical chain oxidation; neither the photolysis of methyl ketones nor of terminal allylic hydroperoxides should contribute to the loss of physical properties (average molecular weight) of the polyolefin.

In the photooxidation of polypropylene, an important reaction is the photolysis of hydroperoxide groups to give alkoxy and hydroxy radicals. Cleavage of the alkoxy radicals then provides the major routes to chain cleavage to give the ketones (A) and (B):

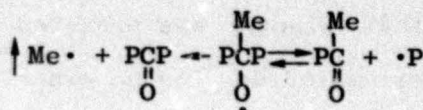


Carlsson and Wiles have studied the photolyses in vacuum of oxidation products of isotactic polypropylene formed both by oxidations in air at 225°^{2a} and by 3750-Å light at 35°.^{2b} In both cases, they conclude that the principal carbonyl products are the ketones A and B, in nearly equal proportions, formed from tertiary alkoxy radicals as indicated above.

- (1) A. M. Trozzolo and F. M. Winslow, *Macromolecules*, 1, 98 (1968).
- (2) J. D. Carlsson and D. M. Wiles, *ibid.*, 2, (a) 587, (b) 597 (1969).

The photooxidation yielded some hydroxyl compounds but the thermal oxidation did not. The formation of ketone (A) is contrary to experience in nonpolymeric systems, where cleavage of a methyl radical from an alkoxy radical is much more difficult than the cleavage of any other alkyl group.³

The simplest explanation for this reported anomalous behavior is that reunion of the polypropylene radical with the methyl polypropylene ketone is favored over diffusion in bulk polymers while the opposite is true for the small methyl radical.



and so the slower reaction is more likely to be complete. A less probable explanation is that photolysis produces a vibrationally excited alkoxy radical which, owing to the rigidity of the solid, cleaves indiscriminately before it can relax by collisional deactivation. Either explanation suggests an important phase effect on alkoxy radical cleavages, and to test these ideas we have carried out some experiments on models for polymer oxy radicals.

(3) J. D. Bacha and J. K. Kochi, J. Org. Chem., 30, 3272 (1965).

4. EXPERIMENTAL

4.1. Materials

t-Amyl hydroperoxide ($t\text{-AmO}_2\text{H}$) was prepared from the alcohol by the procedure of Milas⁴ and distilled to 98% titrimetric purity. Di-t-amyl peroxide ($t\text{-Am}_2\text{O}_2$) and di-t-amylperoxy oxalate (DAPO) were prepared using the procedures of Milas⁴ and Bartlett,⁵ respectively. Although a solution of DAPO in dimethylpentane was quite stable, 1 to 2 g of the neat ester (a viscous liquid, which could not be purified) exploded violently when allowed to warm to room temperature.

1,1-Dinonylethyl alcohol was prepared by adding a threefold excess of methylmagnesium iodide^{6a} to an ether solution of dinonyl ketone.^{6b} After hydrolysis of the magnesium salt with cracked ice, acidification with dilute sulfuric acid, and a washing with bicarbonate and saturated salt solution, the ether was removed, and the product was analyzed by glc. A small amount of starting ketone was present. Column chromatography of the mixture on silica gel with benzene as eluant yielded 8 g of material of 99.9+% purity (only one peak by glc).

1,1-Dinonylethyl hydroperoxide was prepared from the alcohol by the method of Foreman and Lankelma.⁷ Two grams of alcohol was mixed at 0° with 20 ml of glacial acetic acid, 5 ml of 90% hydrogen peroxide, and 1 ml of conc. sulfuric acid. After one hour the mixture was allowed to warm to room temperature, and stirred for an additional three hours. Fifty ml of water was added, and the entire mixture was extracted with

(4) N. A. Milas and D. M. Surgenor, J. Amer. Chem. Soc., 68, 205 (1946).

(5) P. D. Bartlett, et al., ibid., 83, 1762 (1960).

(6) M. S. Kharasch and Otto Reinmuth, Grignard Reactions of Non-Metallic Substances, N. Y., Prentice-Hall, 1954, (a) p. 25, (b) p. 143.

(7) R. W. Foreman and H. F. Lankelma, J. Amer. Chem. Soc., 79, 409 (1957).

three portions of ether. After the mixture was washed with water, bicarbonate, and salt solution and dried with magnesium sulfate, the ether was removed. Iodometric titration of the concentrate indicated 48% hydroperoxide content. Liquid-liquid partition chromatography, using 40% methanol on silica gel as the stationary phase and 2% methanol in benzene as the mobile phase, gave one 0.5-g fraction that titrated for 98% hydroperoxide.⁸

Tetramethylethylene was Eastman White Label, used as received.

The APP used in the photochemical oxidations was PP-N.⁹ For photooxidations solutions were prepared by dissolving approximately 5 wt% in distilled chlorobenzene and adding 10 vol% methanol to provide adequate solubility for the Rose Bengal dye (λ max, 510 nm); no polymer precipitated from solutions.

Polymer films were prepared by evaporation of pentane solvent from solutions of APP⁹ and hydroperoxide, initially with a nitrogen stream, and then under water aspirator, and finally vacuum of 10^{-3} torr. Control films prepared by the same method showed no losses of material on recovery and analysis by glc.

4.2. Photolysis Apparatus

The photochemical apparatus was mounted on an optical bench to facilitate alignment. The source was a Hanovia 400-W mercury lamp with a quartz collimating lens. A water-filled cylindrical filter cell with quartz windows was placed between the lens and the reaction cell to

(8) E. N. Frankel, et. al., J. Am. Oil Chemists' Soc., 38, 134 (1961).

(9) E. Niki, C. Decker, and F. R. Mayo, Report No. 10, SRI Project 8012-1.

remove infrared radiation. The reaction cell was a 3.5-cm-diameter cylindrical cell, 4.0 cm long, with quartz windows, a fritted gas inlet tube on the side, and a 19/20 joint on the top. The total volume of the cell (39 ml) was illuminated. A small condenser on top of the cell minimized loss of volatile solvents. The cell was wrapped with nichrome wire (for heating) and then with sheet polystyrene foam (to assist in maintaining constant ($\pm 1^\circ$) temperature).

For the photooxidation experiments, the cell was connected to a vacuum line (for preliminary evacuation and measurement of pressure) and a gas circulating pump, Bantum Dynavac, model 7062, to circulate oxygen through the solution in a closed system. Oxygen pressure in the system was measured on a Wallace and Tiernan absolute manometer to ± 0.2 torr. The light was filtered with a Corning 3-71 cutoff filter to remove light of < 480 nm.

$t\text{-AmO}_2\text{H}$ or $t\text{-Am}_2\text{O}_2$ were irradiated as solutions in 2,4-dimethylpentane in the apparatus described above, except that the atmosphere was nitrogen and the filter was omitted. Generally, 20 to 30 ml of solution was photolyzed, and small aliquots of solution were removed at intervals for analysis.

Irradiations of dinonylethyl hydroperoxide were run either as solid films prepared as above (Section 4.1.), or as 0.1-M solutions of hydroperoxide in methylcyclohexane in a micro-sized ultraviolet cell (volume = 0.25 ml, path length = 1 mm). The light source was a 200-W PEK point source filtered through a 30-cm water-filled quartz cell and collimated with two quartz lenses.

4.3. Analytical Procedures

Aliquots of solutions of $t\text{-AmO}_2\text{H}$ and $t\text{-Am}_2\text{O}_2$ were removed at intervals for analysis. Part of the aliquot of $t\text{-AmO}_2\text{H}$ was titrated

by the iodometric method of Wibaut;¹⁰ the remainder was reduced with triphenylphosphine¹¹ and analyzed by glc on a 10 ft x 1/4 in. column of 20% Carbowax 20M on Chromsorb P at 75°. Aliquots of t-Am₂O₂ solutions were analyzed directly by glc.

Solutions of dinonylethyl hydroperoxide were recovered from the cell by flushing with three volumes of methylcyclohexane. Polymer films were dissolved in 5 ml of pentane, and pipetted from the cell, which was washed with two additional volumes of pentane. Triphenylphosphine was added in 100% excess to reduce the hydroperoxide to alcohol so that solutions could be analyzed by glc. Analyses for ketones and alcohol were performed on a 10 ft x 1/8 in. 2% Carbowax 20M on Chromsorb G column with temperature programming from 150° to 212°, using bibenzyl as internal standard. Analyses for triphenylphosphine and triphenylphosphine oxide were performed on a 5 ft x 1/8 in. 4% OV-17 Gaschrom Q with temperature programming from 150° to 300°, using bibenzyl as internal standard. Peak areas were determined with an Aerograph Model 470 digital integrator.

5. PHOTSENSITIZED OXIDATION OF APP

Before carrying out photosensitized oxidations with APP, we checked the system by running several experiments with tetramethylethylene¹² as substrate in methanol and methanol-chlorobenzene solvents with Rose Bengal dye as sensitizer. In a typical experiment, 40 ml of 0.2 M tetramethylethylene (8 mmole) in methanol or in 10% methanol-chlorobenzene (vol/vol) containing ~25 mg Rose Bengal sensitizer was placed in the cell, carefully evacuated on the pump to 100 torr, and

(10) J. P. Wibaut, H. B. van Leeuwen, and B. van der Wal, *Rec. Trav. Chim.*, **73**, 1033 (1954).

(11) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Adv. Chem. Series*, **76**, 40 (1968).

(12) D. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3880 (1964).

repressured with oxygen; the procedure was repeated twice to remove air. The oxidation was started by exposing the cell to the light source while circulating the oxygen. In 2 hours the pressure dropped by 200 torr, corresponding to 1.9 mmole of oxygen absorbed. Titration of several aliquots for hydroperoxide gave 2.3 to 2.7 mmole hydroperoxide (none was found in unoxidized olefin). The discrepancy may be due to poor titration end-points in the presence of the dye. Such experiments indicate the ready oxidation of tetramethylethylene in our system and hence the suitability of our system for the photooxidation of a polypropylene solution.

A solution of 47.87 g of 5 wt% APP in chlorobenzene, 3.16 g MeOH, and 20 mg Rose Bengal was photooxidized 6 hours at an initial pressure of 758 torr oxygen at 27°. The oxygen pressure increased slowly to 772 torr at 33°, corresponding to zero absorption of oxygen. No hydroperoxide was detected in the APP solution. Thus singlet oxygen is ineffective in oxidizing purified APP under these conditions.

6. PHOTOLYTIC AND THERMAL CLEAVAGE OF t-AMYLOXY RADICALS

6.1. Photolysis of t-Amyl Hydroperoxide in 2,4-Dimethylpentane (DMP)

We chose DMP as a solvent for these photolyses because it is a low molecular weight model for APP and because we have had previous experience with its oxidation. Some preliminary experiments with the more readily available t-BuO₂H showed that in our system 20% of 0.5 M hydroperoxide disappeared in 1 hour at 50 ± 1°. Results of several experiments with t-AmO₂H, t-Am₂O₂, and DAPO are shown in Table I.

Our experiments on the photolysis of t-AmO₂H in DMP at 50° serve mostly to bring out the complications in the reactions. The t-AmO· radicals produced by irradiation abstract hydrogen atoms from the surrounding medium, and also cleave to equal proportions of acetone

Table I

ABSTRACTION-CLEAVAGE RATIO FOR t-AmO· AND t-BuO·
RADICALS IN DMP^a AT 50° AND 100°

(concentrations in M)

Run	[Source] ₀ , Method	Conversion, %	[t-ROH]	[Me ₂ CO]	Mass ^b Balance, %	k _a /k _d , 1/M
50°						
58	t-AmO ₂ H, 0.0075, photo	86	0.0034	0.0019	73	0.18 ^c
49	t-Am ₂ O ₂ , 0.102, photo	11.5	0.0069	0.0169	101	0.066
53	t-Am ₂ O ₂ , 0.101, photo, Pyrex filter	4.5	0.0039	0.0056	140	~0.1
47	DAPO, 0.089	100	0.072	0.139	118	0.082 0.042 ^d 0.048 ^e
60 ^f	DBPO, 0.10	100	0.16	0.0026	84	9.8
100°						
51	t-Am ₂ O ₂ , 0.10	28	0.0085	0.037	95	0.038
61	t-Bu ₂ O ₂ , ^{1,2} 0.177	16	0.028	0.0032	91	1.45

^a DMP is 6.34 M at 50°, 6.04 M at 100°.^b (t-AmOH + acetone) x 100%/(available t-AmO).^c Assumed average [t-AmO₂H] = 0.004 M equivalent to 0.8 M DMP; equation (1).^{d, e} Corrected for 11.4 wt% t-AmOH^d or t-AmO₂H^e in DAPO.^f At 45°.

and ethyl radicals. However, the t-AmO· and HO· radicals produced by irradiation also induce the free radical chain decomposition of t-AmO₂H to t-AmOH and oxygen. At least part of the oxygen appears in new hydroperoxides, complicating the determination of unreacted t-AmO₂H, and part of the acetone formed is also photolyzed, impairing our material balances and calculations.

Additional low-conversion photolysis experiments with 0.1 to 0.2 M t-AmO₂H have given no better results, but one experiment, run 58,

with 0.0075 M t-AmO₂H, is reported in Table I. It was expected that, at very low concentrations of t-AmO₂H, several of the problems associated with earlier experiments would be minimized. However, the material balance in run 58 is low, and the value of 0.18/M calculated for k_a/k_d from the relation

$$\frac{k_a}{k_d} = \frac{[t-AmOH]}{[M_2O_2CO][DMP]} - \frac{k_a'}{k_d} \frac{[t-AmO_2H]_{av.}}{[DMP]} \quad (1)$$

where

$$\frac{k_a'}{k_d} \sim 200 \frac{k_a}{k_d}$$

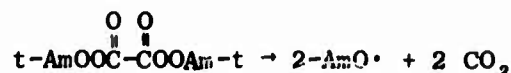
is suspiciously high compared with values obtained in other ways (see below). A major source of error is loss of acetone by photolysis near 300 nm where t-AmO₂H absorbs much less strongly than acetone. This was shown by a blank experiment with 0.004 M acetone in which about half the acetone disappeared during the time of run 58.

6.2. Photolysis of t-Am₂O₂

Although t-Am₂O₂ is a poorer model for hydroperoxidized polypropylene than t-AmO₂H, it is a convenient photochemical source of t-AmO. radicals uncomplicated by most of the problems associated with hydroperoxide. Photolysis of a 0.102 M solution of t-Am₂O₂ for 60 min in nitrogen gave 11% conversion with a good mass balance and $k_a/k_d = 0.066/\underline{M}$ (run 49, Table I). A second experiment with the same initial peroxide solution, but using light filtered through Pyrex to cut off wavelengths < 300 nm, gave a very slow decomposition, poor mass balance, and $k_a/k_d = \sim 0.1/\underline{M}$ (run 53, Table I). Very likely some acetone product photolyzed competitively with the peroxide in this wavelength region.

6.3. Thermal Decomposition of Di-t-Amylperoxy Oxalate (DAPO)

Decomposition of DAPO at 50° is rapid and provides a convenient source of thermally equilibrated t-AmO· radicals for comparison with photochemically generated t-AmO· radicals.



In run 47, Table I, 49.6 mg of DAPO in 1.87 ml DMP was heated for 18 hours (>25 half lives) at 50° in a sealed tube fitted with a break-seal. Gasometric combined with mass spectrometric analyses gave 334 μmoles CO₂; thus the DAPO was 88.4% pure (0.089 M). Glpc analyses for t-AmOH and acetone gave a mass balance of 118% and $k_a/k_d = 0.082/\text{M}$. If all of the 11.6% impurity in DAPO was t-AmO₂H, which analyzed as t-AmOH in glpc, the original solution of DAPO contained 0.035 M t-AmOH or 0.031 M t-AmO₂H, and $k_a/k_d = 0.042/\text{M}$ or 0.048/M, respectively.

6.4. Thermal Decomposition of t-Am₂O₂ at 100°

Because the difference in activation energy between abstraction and cleavage, $E_a = E_d$, governs the change in proportion of these two reactions with changes in temperature and is useful in predicting the behavior of the alkoxy radical system, we also measured k_a/k_d for t-AmO· radicals in DMP at 100° (run 51, Table I). The value of 0.038/M combined with the value at 50° of 0.066/M gives $E_a - E_d = -2.4$ kcal/mole. Although the 50° value is from a photochemical experiment, we believe the differences between photochemical and thermal radicals are small.

Comparable experiments¹³ on t-BuO· radicals in DMP at 50° and 100° give $E_a - E_d = -8.2$ kcal/mole (runs 60 and 61, Table I). Brook¹⁴ reported -8 kcal/mole for t-BuO· radicals in 2,5-dimethylhexane.

(13) A. Allara, K. C. Irwin, and T. Mill, unpublished results.

(14) J.H.T. Brook, Trans. Faraday Soc., 53, 329 (1957).

The difference of about 5.8 kcal/mole between t-BuO· and t-AmO· radicals is surprisingly large, since at 100° the ratio (k_a/k_d) for t-BuO· radicals divided by (k_a/k_d) for t-AmO· radicals is 31 for several hydrocarbons.¹³ This requires that the overall entropy change (A factor) for a t-BuO· radical be 10^{4.9}/sec larger than that for a t-AmO· radical.

7. PHOTOLYTIC CLEAVAGE OF 1,1-DINONYLETHYL HYDROPEROXIDE

Samples were irradiated as solutions or in films for 6 hours. Analysis of residual triphenylphosphine showed that the conversion was about 30% in both cases. Analysis for decomposition products found only ethyl nonyl ketone and 1,1-dinonylethanol as products in both experiments. A part of the alcohol is formed by abstraction of a hydrogen by the tertiary alkoxy radical formed by the decomposing hydroperoxide. The remainder corresponds to the residual hydroperoxide formed by the triphenylphosphine reduction. The ketone is formed by cleavage of the alkoxy radical to give the ketone and a nonyl radical. The solution from the recovered film was carefully checked for traces of dinonyl ketone at sensitivities as much as 80 times as great as that used to analyze for the alcohol and methyl ketone. Even at these high sensitivities no dinonyl ketone could be found.

We have been unable to reconcile our own results on APP with those of Carlsson and Wiles² on isotactic polypropylene. Our Section 6 indicates that a model, t-amyloxy radical, has similar k_a/k_d ratios whether it is prepared by thermal or photolytic decomposition of a peroxide. This Section 7 shows that an alkoxy radical from photolysis of a 19-carbon hydroperoxide cleaves so that only the nonyl radical, not the methyl radical, is lost (within our experimental error). Our previous work^{9,15} on the radical-initiated oxidations of APP in the

(15) C. Decker and F. R. Mayo, Report No. 11, SRI Project 8012-1.

dark does not require any, and cannot allow much, formation of carbonyl groups except those associated with main chain cleavage.

The conclusion of Carlsson and Wiles that substantial proportions of ketone (B) were found in the photolyses in vacuum of previously oxidized films rests on the use of a curve resolver and carbonyl peaks from model carbonyl compounds. While we cannot be sure that their conclusions are erroneous, their acceptance must await photolytic studies of simpler and better defined hydroperoxides and oxidation products, such as those we have made.^{9,15}

8. ACKNOWLEDGMENTS

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